Entanglement and Bell's inequality violation above room temperature in metal carboxilates.

A.M. Souza,[1] D.O. Soares-Pinto,[1] R.S. Sarthour,[1] I.S. Oliveira,[1] M.S. Reis,[2] P. Brandï¿½o,[2] and A. M. dos Santos[3]

[1]*Centro Brasileiro de Pesquisas Fï¿½sicas, Rua Dr. Xavier Sigaud 150, Urca, Rio de Janeiro-RJ 22290-180, Brasil.*
[2]*CICECO, Universidade de Aveiro, 3810-193 Aveiro,Portugal*
[3]*NSSD-MSTD, Oak Ridge National Laboratory, Oak Ridge-TN 37831-6475 USA.*
(Dated: May 30, 2009)

In the present work we show that a special family of materials, the metal carboxylates, may have entangled states up to very high temperatures. From magnetic susceptibility measurements, we have estimated the critical temperature below which entanglement exists in the cooper carboxylate $\{Cu_2(O_2CH)_4\}\{Cu(O_2CH)_2(2\text{-methylpyridine})_2\}$, and we have found this to be above room temperature ($T_e \sim 630$ K). Furthermore, the results show that the system remains maximally entangled until close to ~ 100 K and the Bell's inequality is violated up to nearly room temperature (~ 290 K).

PACS numbers:

INTRODUCTION

Entanglement is the key resource for the majority of applications of the recent growing field of quantum information and quantum computation [1, 2]. This unique quantum phenomenon was until a few years ago thought to exist only in systems with small number of particles at very low temperatures. However, recently it has been discovered that entanglement can also be present in systems containing a large number of particles at finite temperatures [3, 4, 5]. The presence of entangled states in thermal systems has been studied in a few experiments involving magnetic materials [6, 7, 8, 9, 10, 11].

Vlatko Vedral [12] has stated three basic motivations for studying entanglement in many body systems: (i) the need to know the limits of the entanglement, i.e., how large systems can support entanglement and how robust entanglement can be against temperature; (ii) the question whether entanglement can be used as an order parameter for quantum phase transition and, (iii), the need for novel materials which can be used for practical applications in quantum computation and quantum communication. Materials in which robust and useful entangled state can be found naturally could be of great relevance to design quantum solid state devices or as a source of entanglement [13]. By useful entanglement we mean entangled states that can be used to implement quantum protocols, which are more efficient than their classical counterpart. For instance, in quantum cryptography applications and quantum communication complexity tasks, the useful entangled states are those who violate Bell's inequalities [14, 15].

Molecular magnets [16] can be an excellent physical realization of spin chains, providing good opportunities for studying the above topics. In this class of materials, the intermolecular magnetic interactions are extremely weak compared to those within individual molecules. A bulk sample, comprised by a set of non-interacting molecular clusters, is therefore completely described in terms of independent clusters. From a physical point of view, a molecular magnet can combine classical properties found in any macroscopic magnet [16] and quantum properties, such as quantum interference [17] and entanglement [7, 8, 9, 10, 11]. Recently, molecular magnets have been pointed out as good systems to be used in high-density information memories and also, due to their long coherence times [18], in spin based quantum computing devices [19, 20, 21, 22, 23].

The existence of entangled states in molecular magnets is due to the fact that some molecular spin chains can have an entangled ground state. The separation between the ground state and the excited states energies is an important parameter which determine the temperature of entanglement (T_e), i.e. the temperature where the thermal state of the molecular magnet become separable. In the most simple chain, dimers, one can state that stronger is the exchange interaction energy, higher will be T_e [11].

In this paper we show that a special family of molecular magnets (metal carboxylates) can support entanglement above room temperature. We have found in the compound $\{Cu_2(O_2CH)_4\}\{Cu(O_2CH)_2(2\text{-methylpyridine})_2\}$ that $T_e \sim 630$ K. Furthermore, we could also conclude that the system remains in a pure maximally entangled state up to ~ 100 K and the Bell's inequality can be violated up to the room temperature (~ 290 K). This paper is organized as follows: In the next section we give a brief description of the system studied here. The following section contains a study of the entaglement in the compound and in the last section, some commets and conclusions are drawn.
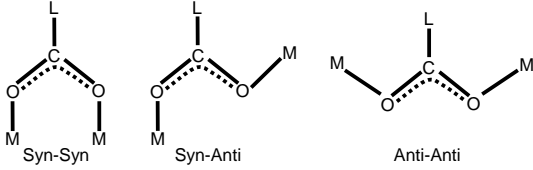
FIG. 1: Metal carboxylate conformation types. Magnetic behavior of this class of materials strongly depends on the conformation type. M means metal and L stands for ligand.

Cu_d-Cu_d	2.631 Å	$Cu-O_m$	1.976 Å
Cu_d-Cu_m	4.689 Å	$O-C-O_d$	127.9^o
Cu_d-O_{ap}	2.120^o	$O-C-O_m$	123.6^o
$\langle\ Cu_d-O_{eq}\ \rangle$	1.978 Å	Cu−Cu (interchain)	8.1055 Å
Cu_d-O-Cu_m	160°		

TABLE I: Selected bond lengths and angles, relevant for the magnetic properties observed for compound $\{Cu_2(O_2CH)_4\}\{Cu(O_2CH)_2(2\text{-methylpyridine})_2\}$. Cu_d - dimer copper, Cu_m - monomer copper, O_{ap} - apical oxigen, O_{eq} - equatorial oxigen.

THE COMPOUND

Metal carboxylates [24, 25, 26, 27] are compounds that can present a wide variety of topologies, compositions, and also allow multiple conformation environments, as shown in Fig.1. A particularly interesting case of conformation in these compounds is the syn-syn. In this structure, a metal poli-carboxylate cluster, usually called paddle-wheel (see figure 2(a)), is formed. These clusters are characterized by a four bridged M-M unit (i.e., a dimer), where the M ions are in square pyramidal coordination with parallel basal planes. The available superexchange pathways observed in these compounds, instead of direct exchange, allows an antiferromagnetic (AF) magnetic exchange (J/k_B) of magnitude in the order of hundreds of degrees. This can be understood by recognizing that the unpaired electron occupies the dx^2-y^2 orbital pointing to the bridging oxygen, while the overlap between dz^2 orbitals is small [28]. The magnetic interaction within the paddle-wheel dimer is therefore consistently both strong and antiferromagnetic, features that allows high entanglement temperatures [11]. Despite their strong intra-dimer interaction, these paddle-wheel compounds may still retain their low dimensional character due to the large distances between the magnetic centers. Conversely, the syn-anti and anti-anti conformations exhibits a rather weak magnetic interaction, that can be either ferromagnetic (FM) or antiferromagnetic, depending mainly on the nature of the ligand (L) and the planarity of the carboxylate group.

Therefore, we have chosen a specific compound, namely $\{Cu_2(O_2CH)_4\}\{Cu(O_2CH)_2(2\text{-methylpyridine})_2\}$, that consists of copper dimer and copper monomers. The dimer is formed by opposing square pyramidal CuO_5. The base oxygens on the adjoining pyramids are part of the four-connecting carboxylate groups in a syn-syn conformation which leads to a strong magnetic interaction between the dimer's atoms. The Cu-Cu distance in this ensemble is 2.63 Å. This square pyramid is slightly distorted form the tetrahedral shape, with an average $O_{ap}-Cu-O_{eq}$ angle of about 95°. The apical oxygen of the pyramid is connected, via another carboxylate group, to the Cu(2-methylpyridine) in a syn-anti configuration. This copper, the monomer, is in a pseudo-octahedral coordination with four oxygens - two from each carboxylate group along the chain and two opposing nitrogen ions from the methyl-pyridine group. These alternating dimers and monomers extend in one direction forming a chain of alternating dimers and monomers (or a syn-syn-anti progression) where the magnetic interaction between the dimer's atoms is strong, and weak between the dimer and the monomer. The 2-methylpyridine groups coordinating the monomeric copper ion act as spacers which are placed alternating along the chain. This large methylpyridine group, as well as the absence of any exchange path between chains, prevents any significant inter-chain magnetic interaction, making this system magnetically one-dimensional down to the lowest measured temperature. The Table (I) lists some selected structural parameters for this compound.

Since the syn-anti magnetic interaction is typically weaker than the syn-syn [29, 30], the magnetic properties of the compound can be modeled considering a superposition of a dimer susceptibility with a Curie-Weiss type susceptibility:

$$\chi = \chi_d + \chi_m. \qquad (1)$$

The first term corresponds to the dimer magnetic susceptibility and for low magnetic fields it is given by [31]:

$$\chi_d = \frac{(g\mu_B)^2}{k_B T}\frac{2}{3+e^{-J/k_B T}}, \qquad (2)$$

where g is the Landï¿$\frac{1}{2}$ factor, μ_B is the Bohr magneton and k_B is the Boltzmann constant. The second term in (1) represents the magnetic susceptibility of the monomer and, since it only interacts with a static magnetic field, its susceptibility just follows the Curie law $\chi_m = C/T$. The experimental results were then fitted according to this model and the parameters were found to be $J/k_B = -693.15$ K, g = 2.21 and $C = 7.02 \times 10^{-5}$ K μ_B FU^{-1} Oe^{-1}. In figure (3) we show a comparison between the model and experimental data.
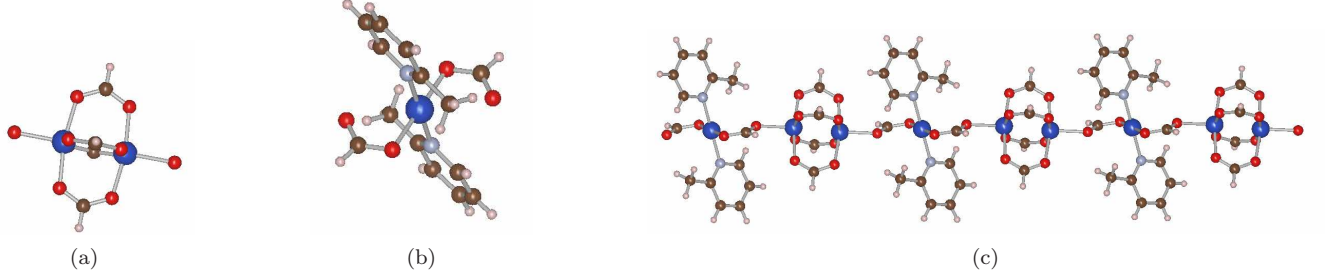
FIG. 2: (Color on line) Detailed view of the structural motifs of {Cu2(O2CH)4}{Cu(O2CH)2(2-methylpyridine)2}. a) Dicopper tetracarboxylate dimer unit. b) Copper dimethyl-pyridine monomeric unit and c) view of the chain formed by alternating dimers and monomers.

ENTANGLEMENT

The task of entanglement quantification is still an open problem in general case (for a recent review see [32]). Hence, usually the detection of entanglement is done using a quantity called *Entanglement Witness* (EW). The concept of Entanglement Witness was first introduced by Horodecki et al. [33]. An EW is an observable which is capable to identify whether a system is in an entangled state. For a spin chain, such a witness can be directly proportional to the magnetic susceptibility [34]:

$$EW(N) = \frac{3k_B T \bar{\chi}(T)}{(g\mu_B)^2 NS} - 1, \qquad (3)$$

where N is the number of spin$-S$ particles and $\bar{\chi}$ is the average of the magnetic susceptibility measured along the three ortogonal directions. For this witness, there will be entanglement in the system if $EW(N) < 0$. In figure 4, the entanglement witness obtained from the measured magnetic susceptibility is shown as a function of the temperature. The witness is negative up to nearly room temperature, showing the presence of entanglement in the system.

To quantify the amount of entanglement in the dimer, we can use a quantity called *Concurrence* [35]. For two qubits described by the quantum state ρ, the concurrence $\mathcal{C}$ is defined as [35]:

$$\mathcal{C} = \max(0, \sqrt{\Lambda_1} - \sqrt{\Lambda_2} - \sqrt{\Lambda_3} - \sqrt{\Lambda_4}), \qquad (4)$$

where Λ's are the eigenvalues of $R = \rho\sigma_y \otimes \sigma_y \rho^* \sigma_y \otimes \sigma_y$, labeled in decreasing order. The degree of entanglement, obtained form this quantity, varies from 0 to 1, and a pair of spins is considered to be in a maximally entangled state if $\mathcal{C} = 1$ and separable when $\mathcal{C} = 0$. For any other values the state of the spins is said to be partially entangled. Using the dimer density matrix ρ_d, it is possible to show that:

$$\mathcal{C} = \max\left[0, -\frac{6}{3 + e^{-J/k_B T}} + 1\right] \qquad (5)$$
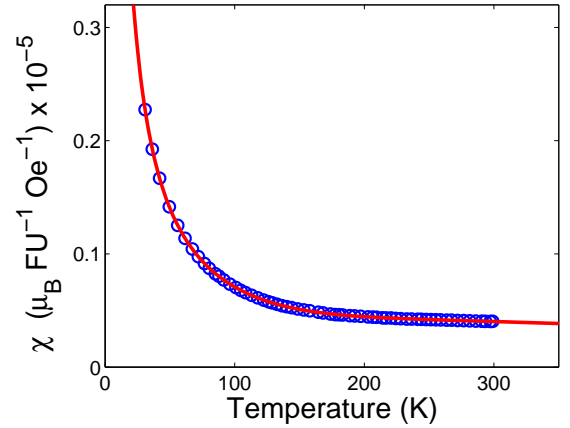

FIG. 3: Magnetic susceptibility as a function of temperature with an applied field of 100 Oe. The points are the experimental results and the solid line is the theoretical prediction, based on the dimer-monomer model, as discussed in the text.

$$= \max\left[0, -\frac{3k_B T(\chi - C/T)}{(g\mu_B)^2} + 1\right] \qquad (6)$$

The equation (6) shows that the concurrence of the dimer is also related to the magnetic susceptibility, which can be obtained experimentally. On figure 5 the concurrence calculated according to the equation (6) is shown, and the solid line is the theoretical prediction of the equation (5) with parameters g, J, and C obtained from the fit to the experimental susceptibility (see Fig. 4). An interesting result is that the spins of the dimer remain maximally entangled up to ~ 100 K. From equation (5), we can estimate the critical temperature below which entanglement exists as being $T_e = -J/k_B \ln(3) \sim 630$ K, which is well above room temperature. It is important to emphasize that the high value of the exchange integral J is due to the syn-syn conformation and thus any material with such kind of conformation are strong candidates to contain entanglement at high temperatures.
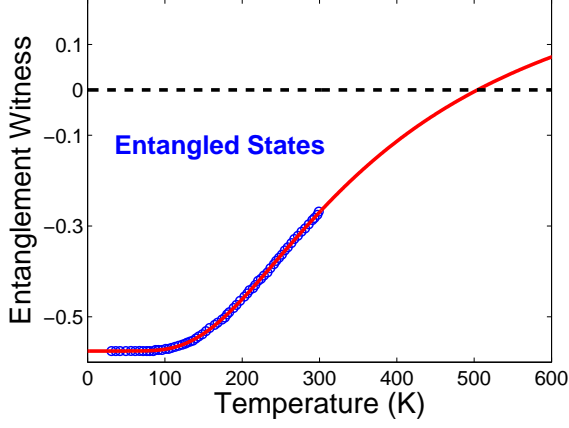
FIG. 4: Experimental entanglement witness derived from the magnetic susceptibility measurements. The points are the experimental results and the solid line is the theoretical prediction, based on the dimer-monomer model, as discussed in the text.
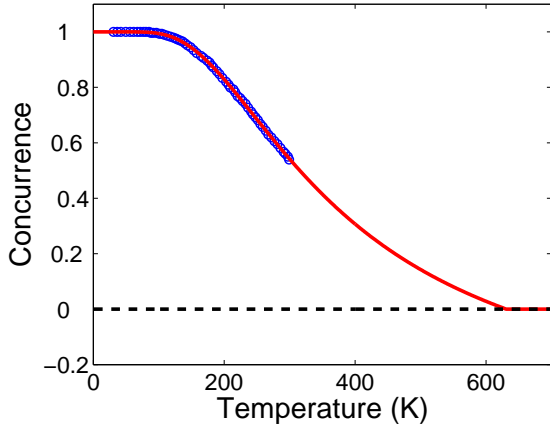

FIG. 5: Concurrence as a function of temperature. The points are the experimental results and the solid line is the theoretical prediction, based on Eq. (5).

The violation of Bell's inequalities is of great importance to quantum information science. These inequalities are closely related to the usefulness of entangled states [14, 15]. In particular, Bell's inequalities violations are related to the security of cryptography protocols [15] and are a necessary and sufficient condition to the usefulness of quantum states in communication complexity protocols [14]. A Bell's inequality test for two qubits involves measurements of a set of correlations functions, which for a magnetic system are the correlations of the magnetic moments along specific directions [36]. For a system with two spin 1/2, the test involves the measurement of the
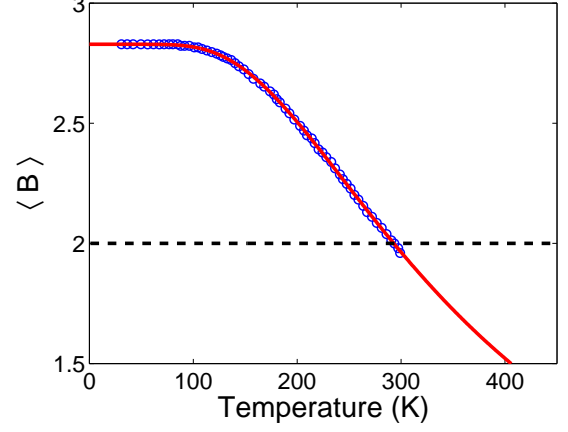

FIG. 6: The mean value of the Bell operator as a function of temperature. The points are the experimental results and the solid line is the theoretical prediction, based on Eq. (8).

mean value of the Bell operator given by:

$$\mathcal{B} = \vec{n}_1 \cdot \vec{\sigma} \otimes (\vec{n}_2 \cdot \vec{\sigma} - \vec{n}_4 \cdot \vec{\sigma}) + \vec{n}_3 \cdot \vec{\sigma} \otimes (\vec{n}_2 \cdot \vec{\sigma} + \vec{n}_4 \cdot \vec{\sigma}) \quad (7)$$

In the above equation, $\vec{n} \cdot \vec{\sigma}$ is the projection of the spin in the direction $\vec{n}$. For any separable state, the mean value of Eq. (7) satisfies the relation $|\langle \mathcal{B} \rangle| \leq +2$, and whenever this inequality is violated, the system is in an entangled state [37]. There is a particular set of directions for which the violation reaches its maximum. The ground state of an antiferromagnetic dimer violates maximally the Bell's inequality if we choose $\vec{n}_1$, $\vec{n}_2$, $\vec{n}_3$ and $\vec{n}_4$ as being $(0, 0, -1)$, $(-1, 0, -1)/\sqrt{2}$, $(-1, 0, 0)$ and $(-1, 0, 1)/\sqrt{2}$, respectively. Then, using this set of directions, the Bell operator becomes: $\mathcal{B} = \sqrt{2}(\sigma_z \otimes \sigma_z + \sigma_x \otimes \sigma_x)$. Using the dimer density matrix, ρ_d, to calculate the correlations $\langle \sigma_z \otimes \sigma_z \rangle$ and $\langle \sigma_x \otimes \sigma_x \rangle$, it is easy to show that:

$$|\langle \mathcal{B} \rangle| = 4\sqrt{2} \left| \frac{2}{3 + e^{-J/k_B T}} - \frac{1}{2} \right| \quad (8)$$

$$= 4\sqrt{2} \left| \frac{k_B T (\chi - C/T)}{(g\mu_B)^2} - \frac{1}{2} \right| \quad (9)$$

From equation (9), it is possible to verify whether the entangled state of the system violates the Bell's inequality or not. On figure 6, the mean value of the Bell operator as a function of the temperature is shown, along with its theoretical prediction. From the figure 6, we see that the Bell's inequality is violated below ~ 290 K and maximum violation is observed for temperatures below ~ 100 K, which is compatible to the previous result, obtained from the concurrence, i.e., the system remains maximally entangled up to ~ 100 K).

CONCLUSION

In summary, we identified a family of magnetic materials that can support entanglement at very high temperatures, namely metal carboxylates with syn-syn conformation. As an example, we choose the compound $\{Cu_2(O_2CH)_4\}\{Cu(O_2CH)_2(2\text{-}$ methylpyridine$)_2\}$, and for this material we determine that the critical temperature below bipartite entanglement exist is $T_e \sim 630$ K. Furthermore, we could also conclude that the system remains maximally entangled up to ~ 100 K and the Bell's inequality can be violated up to close room temperature (~ 290 K), which is a special feature of this material, since Bell's inequalities are of great importance to Quantum Computation [14, 15]. The critical temperature estimated in this work is the highest value reported in the literature and the identification of this class of materials can open the way doors for new researches toward a solid state quantum devices. In addition, we are convinced that other systems can support entanglement at even higher temperatures, since exchange magnetic coupling as high as that provided here has been reported in the literature [38].

[1] M. A. Nielsen and I. L. Chuang, *Quantum Computation and Quantum Information* (Cambridge University Press, Cambridge, 2000).

[2] I. S. Oliveira, T. J. Bonagamba, R. S. Sarthour, J. C. C. Freitas, and E. R. deAzevedo, *NMR Quantum Information Processing* (Elsevier, Copenhagen, Neatherland, 2007).

[3] M. C. Arnesen, S. Bose, and V. Vedral, Phys. Rev. Lett. **87**, 017901 (2001).

[4] L. Amico, R. Fazio, A. Osterloh, and V. Vedral, Rev. Mod. Phys. **80**, 517 (2008).

[5] D. Markham, J. Anders, V. Vedral, M. Murao, and A. Miyake, Europhys. Lett. **81**, 40006 (2008).

[6] S. Ghosh, T. F. Rosenbaum, G. Aeppli, and S. N. Coppersmith, Nature **452**, 48 (2003).

[7] Č. Brukner, V. Vedral, and A. Zeilinger, Phys. Rev. A **73**, 012110 (2006).

[8] T. G. Rappoport, L. Ghivelder, J. C. Fernandes, R. B. Guimarães, and M. A. Continentino, Phys. Rev. B **75**, 054422 (2007).

[9] T. Vértesi and E. Bene, Phys. Rev. B **73**, 134404 (2006).

[10] A. M. Souza, M. S. Reis, D. O. Soares-Pinto, I. S. Oliveira, and R. S. Sarthour, Phys. Rev. B **77**, 104402 (2008).

[11] D. O. Soares-Pinto, A. M. Souza, R. S. Sarthour, I. S. Oliveira, M. S. Reis, P. B. ao, and A. M. dos Santos, Submitted to New J. Phys. (2008).

[12] V. Vedral, Nature **453**, 1004 (2008).

[13] G. D. Chiara, Č. Brukner R. Fazio, G. M. Palma, and V. Vedral, New J. Phys. **8**, 95 (2006).

[14] Č. Brukner, M. Żukowski, J. W. Pan, and A. Zeilinger, Phys. Rev. Lett. **92**, 127901 (2004).

[15] A. Acín, N. Gisin, and L. Masanes, Phys, Rev. Lett. **97**, 120405 (2006).

[16] L. Bogani and W. Wernsdorfer, Nature Materials **7**, 179 (2008).

[17] C. M. Ramsay, E. del Barco, S. Hill, S. J. Shah, C. C. Beedle, and D. N. Hendrickson, Nature Physics **4**, 277 (2008).

[18] A. Ardavan, O. Rival, J. J. L. Morton, S. J. Blundell, A. M. Tyryshkin, A. Timco, and R. E. P. Winpenny, Phys. Rev. Lett. **98**, 057201 (2007).

[19] M. Affronte, I. Casson, M. Evangelistia, A. Candini, S. Carretta, C. Muryna, S. Teat, G. Timcoa, W. Wernsdorfer, and R. Winpenny, Angew. Chem. Int **44**, 6496 (2005).

[20] F. Troiani, M. Affronte, S. Carretta, P. Santini, and G. Amoretti, Phys. Rev. Lett **94**, 190501 (2005).

[21] F. Troiani, A. Ghirri, M. Affronte, S. Carretta, P. Santini, G. Amoretti, S. Piligkos, G. Timco, and R. E. P. Winpenny, Phys. Rev. Lett **94**, 207208 (2005).

[22] F. Michael, N. Leuenberger, and D. Loss, Nature **410**, 789 (2001).

[23] J. Lehmann, A. Gaita-Ario, E. Coronado, and D. Loss, Nature Nanotechnology **2**, 312 (2007).

[24] C. N. R. Rao, S. Natarajan, and R. Vaidhyanathan, Angew. Chem. Int. Ed. **43**, 1466 (2004).

[25] R. E. Sesto, L. Deakin, and J. S. Miller, Synthetic Metals **122**, 543 (2002).

[26] S. J. Blundell and F. L. Pratt, J. Phys.: Condens. Matter **16**, R771 (2004).

[27] V. Calvo-Pérez, A. Vega, and E. Spodine, Organometallics **25**, 1953 (2006).

[28] A. Rodríguez-Fortea, P. Alemany, S. Alvarez, and E. Ruiz, Chem. Eur. J. **7**, 627 (2001).

[29] E. Colacio, J. M. Dominguez-Vera, J. P. Costes, R. Kivekas, J. P. Laurent, J. Ruiz, and M. Sundberg, Inorg. Chem. **31**, 774 (1992).

[30] B. Żurowska, J. Mroziński, and Z. Ciunik, Polyhedron **26**, 3085 (2007).

[31] O. Khan, *Molecular Magnetism* (Wiley-VCH, New York, 1993).

[32] R. Horodecki, P. Horodecki, M. Horodecki, and K. Horodecki, Accepted in Rev. Mod. Phys. (2008).

[33] M. Horodecki, P. Horodecki, and R. Horodecki, Phys. Lett. A **223**, 1 (1996).

[34] M. . Wieśniak, V. Vedral, and Č. Brukner, New. J. Phys. **7**, 258 (2005).

[35] W. K. Wootters, Phys. Rev. Lett. **80**, 2245 (1998).

[36] A. M. Souza, A. Magalhães, J. Teles, E. R. deAzevedo, T. J. Bonagamba, I. S. Oliveira, and R. S. Sarthour, New J. Phys. **10**, 033020 (2008).

[37] M. Genovese, Phys. Rep. **413**, 319 (2005).

[38] N. Motoyama, H. Eisaki, and S. Uchida, Phys. Rev. Lett.

76, 3212 (1996).